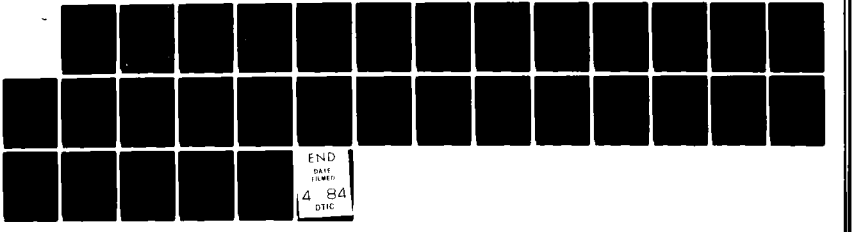
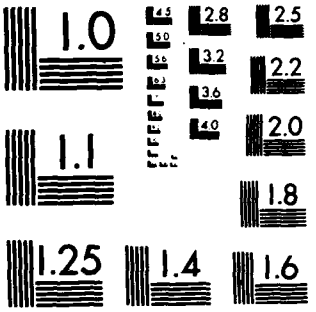
AD-A139 021 INTRAMOLECULAR ELECTRON TRANSFER AT METAL SURFACES I 1/1
RELATIVE ENERGETICS O..(U) PURDUE UNIV LAFAYETTE IN
DEPT OF CHEMISTRY S W BARR ET AL. NOV 83 TR-23
UNCLASSIFIED N00014-79-C-0670 F/G 7/4 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A139021

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0670

TECHNICAL REPORT No. 23

Intramolecular Electron Transfer at Metal Surfaces I. Relative Energetics of Some Corresponding Outer- and Inner-Sphere Pathways Involving Halide and Pseudohalide Bridging Ligands

by

Stephen W. Barr and Michael J. Weaver

Prepared for Publication

in

Inorganic Chemistry

Department of Chemistry

Purdue University

West Lafayette, IN 47907

November 1983

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

DTIC FILE COPY

DTIC ELECTE MAR 16 1984 S D E

84 03 15 170

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: Technical Report No. 23 — 2. GOVT ACCESSION NO.: AD-A139021	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Intramolecular Electron Trasnfer at Metal Surfaces I. Relative Energetics of Some Corresponding Outer- and Inner-Sphere Pathways Involving Halide and Pseudohalide Briding Ligands	5. TYPE OF REPORT & PERIOD COVERED: Technical Report No. 23 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Stephen W. Barr and Michael J. Weaver	8. CONTRACT OR GRANT NUMBER(s): N00014-79-C-0670
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Purdue University, West Lafayette, IN 47907	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, Arlington, VA 22217	12. REPORT DATE: November 1983 13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Intramolecular electron transfer, gold, platinum electrode, cobalt(III) reduction, ligand-induced adsorption

K sub et Ret Sec

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The electroreduction kinetics of a number of Co(III) ammine and ethylenediamine complexes containing chloride, bromide, and isothiocyanate ligands have been studied at platinum- and gold-aqueous interfaces in order to investigate the consequences of attaching simple transition-metal reactants to electrocatalytic metal surfaces upon the electron-transfer energetics. The virtues of evaluating unimolecular rate constants k_{et} (sec^{-1}) for comparing the energetics of electrochemical inner- and outer-sphere pathways are pointed out.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Values of k_{et} for inner-sphere electron transfer, k_{et}^{is}, were obtained by combining apparent rate constants k_{app} for the overall reaction with measurements of the reactant surface concentration. Estimates of k_{et} for the same reactions occuring via outer-sphere pathways, k_{et}^{os}, were extracted from the measured values of k_{app} at iodide-coated platinum surfaces and from the rate constants obtained using homogeneous outer-sphere reductants. For halide-bridged reactions, $k_{et}^{is} \geq k_{et}^{os}$, whereas the isothiocyanate-bridged reactions, $k_{et}^{is} \leq k_{et}^{os}$. Likely reasons for these greater bridging efficiencies with the halide ligands are sought in terms of electronic coupling effects between the redox center and the metal surface, and also in the anticipated differences of reactant orientation between the inner- and outer-sphere transition states.

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1
DTIC COPY INSPECTED

INTRODUCTION

A fundamental question in electrochemical kinetics concerns the various ways in which the chemical nature of the electrode material may influence the energetics of electron transfer. The simplest class of electrode reactions involves redox couples of the form

$$Ox + e^- \text{ (electrode)} \rightleftharpoons Red \qquad (1)$$

where both the oxidized and reduced forms (Ox and Red, respectively) are solution species, so that the electrode material is not involved in the reaction stoichiometry. Such electrode processes can take place via an "outer-sphere" route where the reactant is excluded from the inner layer of solvent molecules adjacent to the electrode surface. For such pathways the electrode surface may exhibit little specific influence upon the transition-state stability. However, many electrode reactions are thought to proceed via "inner-sphere" mechanisms where the reactant, or its coordinated ligands, are bound directly to the surface in the transition state for electron transfer. Although the kinetics of such "strong interaction" pathways will clearly be sensitive to the chemical composition of the electrode, little attention has been devoted to examining the matter and extent to which metal surfaces may perturb the electron-transfer energetics, i.e., act as "electrocatalysts."

Electrochemical,[2,3] as well as homogeneous,[4] electron-transfer reactions can be considered to occur in two steps, involving the formation of a precursor intermediate having the appropriate configuration at the interface that subsequently undergoes thermal activation leading to electron transfer. It is useful to distinguish between influences of the metal surface upon the reaction energetics arising from changes in the activation barrier for the elementary electron-transfer step itself, from those merely due to variations in the stability of the precursor state, i.e. in the cross-sectional reactant concentration at the electrode surface.[2,3] Such a separation can be made by expressing the "apparent" rate constant for the overall reaction, k_{app}, as[3]

$$k_{app} = K_p k_{et} \qquad (2)$$

where K_p is the equilibrium constant for forming the precursor state from the bulk reactant, and k_{et} is the rate constant for the elementary electron-transfer step. For inner-sphere electrochemical reactions, the precursor state can often be sufficiently stable to enable values of k_{et} to be measured directly.[2,5,6] Such "intramolecular" rate parameters have been obtained for a number of homogeneous inner-sphere reactions in the last several years;[7] measurements for organic-bridged systems have provided important insights into the factors influencing electron transfer through extended structural units.[7,8]

Despite the burgeoning interest in the electrochemistry of adsorbed (or "surface-attached") molecules, analogous data for electrochemical inner-sphere processes; i.e. rate constants for mechanistically simple electron transfer processes involving surface-bound reactants, are sparse.[5,6,9] We have been exploring suitable electrochemical systems and measurement strategies to enable values of k_{et} to be obtained for transition-metal reactants bound to metal surfaces via a variety of inorganic and organic bridging ligands. Such processes are entirely analogous to intramolecular electron-transfer reactions within binuclear transition-metal complexes, the metal surface being substituted for one of the metal redox centers. These reactions can therefore be perceived as involving "surface intramolecular" electron transfer. Following the well-known studies of homogeneous redox processes, we have selected for detailed scrutiny reactions involving the one-electron reduction of Co(III) and Cr(III). The virtues of these reactant systems are well known to inorganic kineticists:[7,10] the substitution inertness of the metal centers enable stable complexes containing a variety of coordinated ligands to be prepared, and the substitution lability and instability of the products facilitates measurements of the kinetics of the forward reaction.

Of central interest is the manner and extent to which the energetics of the elementary electron-transfer step are sensitive to the structure of the bridging group and the nature of the metal surface. Providing that the reactant-surface binding is strong, the reactant concentration in the adsorbed precursor state can be directly determined.[2,5] Values of k_{et} can then be obtained either from parallel measurements of K_p and k_{app} for inner-sphere pathways, or directly from the current for reduction (or oxidation) of a known adsorbate concentration using a suitable pulse technique.[2,5,6] In addition to the structurally well-defined mercury surface, we have selected platinum, gold, silver and copper electrodes for detailed study.[2,6] One reason for this choice is that a variety of coordinated ligands bind strongly to these surfaces.

Broadly speaking, electrochemical kinetics data have been gathered with the following related aims in mind: (i) the comparison between the kinetics of the same, or related, reactions occurring via inner- and outer-sphere pathways; (ii) the effect of altering the metal electrode composition upon k_{et} and K_p; (iii) the sensitivity of k_{et} to the structure of the bridging ligand. We have recently discussed the fundamental significance of such comparisons, and their utility for examining the influences of reactant-electrode interactions upon electrochemical reactivity.[2a,3] We have shown that the "preequilibrium" treatment [Eq (2)] can be applied to outer-, as well as inner-sphere, electrochemical reactions by estimating K_p for the former process using a simple statistical model.[3a] This enables values of k_{et} to be obtained for both types of reaction pathways, so that the influence of reactant-surface interactions upon k_{et} can be assessed in a particularly direct manner.[3a]

Kinetic data for a number of representative "surface intramolecular" electron transfer processes are presented and discussed in this and the following article[11a] which deal with inorganic ligand bridges. Another article, appearing elsewhere, deals with systems containing extended organic bridges.[11b] A summary article

will also be available.[12] These studies constitute the first systematic examination of electron-transfer kinetics involving simple surface-attached reactants. In the present paper (Part I), electrochemical kinetics data are reported for the reduction of a number of Co(III) ammine and ethylenediammine complexes containing simple anionic bridging ligands, primarily at platinum and gold surfaces. Reactants containing chloride, bromide, or isothiocyanate bridging ligands are examined in order to compare the catalytic properties of monoatomic and polyatomic bridging anions. By comparing values of k_{et} obtained for these inner-sphere processes with rate constants for corresponding outer-sphere pathways, we have been able to assess the consequences of surface attachment upon the electron-transfer energetics.

EXPERIMENTAL

Most Co(III) complexes were synthesized as the solid perchlorate salts using the following literature procedures: $Co(NH_3)_6^{3+}$,[13] $Co(NH_3)_5OH_2^{3+}$,[14] $Co(NH_3)_5F^{2+}$,[14] $Co(NH_3)_5Br^{2+}$,[15] $Co(NH_3)_5Cl^{2+}$,[14] $Co(NH_3)_5NCS^{2+}$,[16] $Co(NH_3)_5OAc^{2+}$ [17] (OAc = acetate), $c\text{-}Co(en)_2NCS)_2^{+}$,[18] (en = ethylenediamine), $c\text{-}Co(en)_2Cl_2^{+}$,[19] and $c\text{-}Co(NH_3)_4Cl_2^{+}$.[20] A supporting electrolyte of 0.1 M $NaClO_4$ + 5 mM $HClO_4$ was used for most electrochemical kinetics measurements. Sodium perchlorate was thrice recrystallized from water. The perchloric acid was added to buffer the pH to sufficiently low values to avoid the precipitation of the Co(II) reduction product on the electrode surface.[21] The electrochemical kinetics parameters were generally found to be independent of pH in the range pH 2-3. Water was purified by double distillation from alkaline permanganate, followed by passage through an all-quartz "non-boiling" still (Dida-Science, Montreal).

Most of the procedures and apparatus employed have been outlined in other papers from this laboratory.[2c,6,11,22] The platinum and gold electrodes were fabricated as rotating disk electrodes sheathed in Teflon. They were pretreated

immediately prior to the experiment by means of mechanical polishing followed by conventional electrochemical cycling procedures in 0.1 M $HClO_4$.[2c,22]

Measurements of apparent rate constants k_{app} as a function of electrode potential E at platinum and gold were made chiefly using rotating disk voltammetry and/or normal pulse polarography with a rotating electrode as described in the following article.[11a] Rate data at mercury were obtained with a dropping electrode using normal pulse polarography. Reactant concentrations were normally 1-2 mM. Apparent rate constants for some reactions were obtained using linear sweep voltammetry with sweep rates in the range 100-500 mV sec^{-1}, employing the data analysis method outlined in ref. 23. All the Co(III) reduction reactions are entirely irreversible since $Co(OH_2)_6^{2+}$ is rapidly formed from the substitutionally labile Co(II) product, whose reoxidation is thermodynamically unfavorable except at extremely positive electrode potentials.[21] The values of k_{app} between replicate runs were normally reproducible at least to within ±50%, although they usually decreased slowly with time. Rate data were therefore gathered usually within a few minutes after the electrode activation procedure. Measurements were restricted to potential regions where the electrode surfaces were free of oxide or hydrogen films or other background currents, as deduced from cyclic voltammetry.[22] Direct measurements of surface rate constants k_{et} for some reactions were made using rapid linear sweep voltammetry (sweep rates 10-50 V sec^{-1}) using bulk reactant concentrations ≤ 100 μM as described in ref. 11. Electrode potentials were measured with respect to a saturated calomel electrode (s.c.e.), and all measurements were performed at 24 ± 0.5°C.

RESULTS AND MECHANISTIC ANALYSES

Inner-Sphere Pathways

Table I summarizes kinetics data for the reduction of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5NCS^{2+}$ at platinum and gold surfaces in contact with

0.1 M $NaClO_4$ + 5 mM $HClO_4$; Table II gives corresponding data for the reduction of c-$Co(en)_2Cl_2^+$, c-$Co(NH_3)_4Cl_2^+$, and c-$Co(en)_2(NCS)_2^+$. The reactions listed in Tables I and II are expected to involve monobridged and dibridged inner-sphere transition states, respectively. The rate data are conveniently summarized as values of k_{app} at a given electrode potential, with the potential dependence of k_{app} expressed as an apparent transfer coefficient α_{app} [$= -(RT/F)(\partial \ln k_{app}/\partial E)$]. It is desirable to compare the rate constants for a given electrochemical reaction occurring by different reaction mechanisms or at different surfaces by using a fixed electrode potential.[2c,21] The electrode potentials to which the rate constants in Tables I and II refer; 300 mV and 0 mV for the halide and thiocyanate complexes, respectively, were chosen so to minimize the extent of data extrapolation that was required. The values of k_{app} are the average of at least four determinations and are generally precise to within ±25%. The attainment of such reproducibility required careful attention to the electrode surface preparation and extensive purification of the reagents used.[2c,22] A number of other reactions at platinum and gold, such as those for reactants containing azide ligands, were found to yield insufficiently reproducible rate parameters[24] and therefore are omitted from Tables I and II.

Strong evidence that these reactions proceed via rate-dominating inner-sphere pathways at platinum and gold surfaces is available from several sources. The addition of ca. 5 mM iodide yields striking (ca. 10^5- to 10^6-fold) rate decreases for $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, c-$Co(NH_3)_4Cl_2^+$, and c-$Co(en)_2Cl_2^+$ reduction (Tables I, II).[2c] This contrasts the large rate increases resulting from iodide specific adsorption that are observed for such cationic complexes reacting by outer-sphere pathways.[2b,25] It is likely that these rate decreases are due to the elimination of surface coordination sites by the iodide which is adsorbed to a

monolayer at platinum and gold under these conditions.[2c,26] [These iodide-coated surfaces are labeled PtI and AuI in Tables I and II, and below.]

This method of mechanism diagnosis yielded less persuasive results for the reduction of $Co(NH_3)_5NCS^{2+}$ and c-$Co(en)_2(NCS)_2^+$, since only small rate decreases were observed upon iodide addition at both platinum and gold surfaces (Tables I, II). This is probably due to the ability of the thiocyanate bridging ligand to compete effectively with iodide for surface coordination sites. However, further evidence of inner-sphere mechanisms for the thiocyanate- as well as halide-containing complexes is deduced from the observation that the electrochemical reaction orders m [$= (\partial \ln i/\partial \ln C_r)_E$] are substantially below unity for all these reactions at clean platinum and gold (Table III). (The reaction orders were determined using rotating disk voltammetry for reactant concentrations C_r in the range ca. 0.1 - 1 m$\underline{M}$. Variations in C_r for a given bulk reactant concentration were obtained by altering the electrode rotation speed and hence the extent of concentration polarization at a fixed electrode potential.[2b,22]) Since the reaction rate and hence i should generally be proportional to Γ_p rather than to C_r, these fractional reaction orders are indicative of reactant surface concentrations Γ_p that approach saturation, i.e. a monolayer. In contrast, the reduction of $Co(NH_3)_5OH_2^{3+}$, for example, yields values of m close to unity (Table III), as expected for an outer-sphere pathway having much smaller values of Γ_p, so that C_r is proportional to Γ_p.

In several cases the occurrence of inner-sphere reduction pathways can be implied by the direct determination of the surface concentration Γ_p of the specifically adsorbed intermediate using rapid linear sweep voltammetry. This technique involves the determination of the charge contained under the cathodic voltammetric peak using sufficiently small bulk reactant concentrations ($\lesssim$ 0.1 m$\underline{M}$) and high sweep rates (10-50 V sec^{-1}) so that current due to reduction of the diffusing reactant contributes negligibly to this faradaic charge. The analysis procedure is detailed elsewhere.[6,11a] Although a number of attempts were made to obtain values of

Γ_p at platinum and gold surfaces using single potential-step chronocoulometry, unreasonably small or even negative estimates of Γ_p were obtained.[6] Similar results were also obtained at silver electrodes;[11a] the origins of these difficulties are discussed elsewhere.[6]

Representative values of Γ_p for Co(III) reactants at platinum and gold obtained by rapid linear sweep voltammetry are summarized in Table IV. Due to the assumptions contained in the analysis employed,[6] these results should be regarded as only approximate. Nevertheless, Γ_p was found to be almost independent of the bulk reactant concentration C_r and the initial potential E_i, indicating that the reactant coverages approaches a monolayer even at the small values of C_r ($\lesssim$ 0.1 mM) for which this technique can be employed. The larger values of Γ_p obtained for $Co(NH_3)_5Cl^{2+}$ (4×10^{-10} mole cm^{-2}) compared with those for $Co(NH_3)_5NCS^{2+}$ and $c\text{-}Co(en)_2(NCS)_2^+$ ($2 - 2.5 \times 10^{-10}$ mole cm^{-2} (Table IV)) are understandable in view of the smaller area occupied by the chloride compared with isothiocyanate bridging ligands. (There are about 2×10^{-9} mole of surface metal atoms per cm^2 at a smooth platinum or gold surface,[27] corresponding to about 5 and 9 metal atoms per adsorbed chloride and isothiocyanate complex, respectively.)

Well-defined cathodic voltammetric peaks could not be obtained for several adsorbed reactants [$Co(NH_3)_5Cl^{2+}$ and $c\text{-}Co(NH_3)_4Cl_2^+$ at gold; $Co(NH_3)_5NCS^{2+}$, $c\text{-}Co(en)_2(NCS)_2^+$, and $c\text{-}Co(NH_3)_4Cl_2^+$ at platinum] for which strong adsorption is expected.[28] However, the observation of fractional reaction orders for the reduction of these complexes (Table III) suggests that they are adsorbed in amounts approaching a monolayer at platinum and gold at the reactant concentrations (ca. 1 mM) employed for the kinetics measurements.

Having obtained estimates of Γ_p for the inner-sphere reactions given in Tables I and II, values of K_p corresponding to the listed values of k_{app} can be obtained from $K_p = \Gamma_p/C_r$.[30] These enable rate constants for the elementary

electron-transfer step, k_{et}^{is}, to be extracted using Eq. (2). (Equivalently, k_{et}^{is} can be obtained directly from $k_{et}^{is} = i/F\Gamma_p$,[11a] where i is the faradaic current density for reduction of an adsorbate concentration Γ_p.) The resulting values of k_{et}^{is} are listed in Tables I and II, along with values of k_{app}, K_p and k_{et}^{is} determined for $Co(NH_3)_5NCS^{2+}$ and c-$Co(en)_2(NCS)_2^+$ reduction at silver and mercury electrodes.[2a,11a,40]

Experimental values of k_{et}^{is} could also be obtained directly from the rapid linear sweep voltammograms used to obtain Γ_p. The analysis procedure is described elsewhere.[11] The resulting values of k_{et}^{is} for $Co(NH_3)Cl^{2+}$ reduction at platinum and $Co(NH_3)_5NCS^{2+}$ reduction at gold are also given in Table I, and c-$Co(en)_2(NCS)_2^+$ at gold and silver electrodes in Table II, each listed in italics. Similarly to the corresponding data for Cr(III) reduction at silver electrodes,[11] these values of k_{et}^{is} are comparable to, yet slightly (ca. two-fold) larger than, the corresponding values obtained indirectly from k_{app} and K_p. The estimated uncertainties in k_{et}^{is} are no greater than a factor of two.

Outer-Sphere Pathways

There is evidence that the iodide-coated platinum and possibly gold electrodes induce rate-determining outer-sphere pathways for normally inner-sphere reactions by effectively denying the potential bridging ligands access to the surface coordination sites.[2b] This is deduced in part by comparing the electrochemical reactivities with those for homogeneous reduction of the same reactants by outer-sphere reagents (vide infra).

The measured apparent rate constants for $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5NCS^{2+}$ reduction at iodide-coated platinum electrodes were utilized to estimate values of k_{et} for the outer-sphere pathways, k_{et}^{os}, using the relation [3a]

$$k_{et}^{os} = k_{corr}/\delta r \qquad (5)$$

where k_{corr}^{os} is the work-corrected rate constant and δr is the effective reaction zone thickness (probably $\sim 1\text{Å}$ [3a]). The double-layer correction required to obtain values of k_{corr}^{os} from the measured values of k_{app} were obtained by using $Co(NH_3)_5F^{2+}$

reduction as a "kinetic probe". This reaction occurs via a well-defined outer-sphere pathway at mercury,[21] enabling values of k^{os}_{corr} to be obtained.[32] Since $Co(NH_3)_5F^{2+}$ has the same charge and a similar structure to $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5NCS^{2+}$, values of k^{os}_{corr} for the latter reactants can be obtained simply from

$$(k^{os}_{corr}/k^{os}_{app})_E = (k^{F}_{corr}/k^{F}_{app})_E \qquad (6)$$

where k^{F}_{corr} and k^{F}_{app} are the double-layer corrected rate constant at mercury, and the apparent rate constant at iodide-coated platinum, respectively, for $Co(NH_3)_5F^{2+}$ reduction at a given electrode potential E. Appropriate values of k_{app}, along with the corresponding estimates of k^{os}_{et} resulting from Eqs. (5) and (6) with $\delta r = 1\text{Å}^{o}$ are listed in Table I.[33] For each reaction, the corresponding values of k^{is}_{et} and k^{os}_{et} refer to a common electrode potential.

An alternative method for estimating values of k^{os}_{et} for normally inner-sphere electrochemical reactions utilizes rate data for the homogeneous reduction of the same reactants by simple one-electron reagents, such as $Ru(NH_3)_6^{2+}$, that are known to induce outer-sphere pathways.[12] This approach relies on the following relationship[2c,12,21] which is deduced from the conventional model for outer-sphere electron transfer:[34]

$$k^{os}_{et,1} = (k_{h,1}/k_{h,2})_R \cdot k^{os}_{et,2} \qquad (7)$$

where $k^{os}_{et,1}$ and $k^{os}_{et,2}$ are unimolecular rate constants for the electrochemical reduction (or oxidation) of a pair of reactants at a given electrode potential, and $k_{h,1}$ and $k_{h,2}$ are second-order rate constants for the homogeneous reduction (or oxidation) of the same two reactants by a fixed outer-sphere reagent R. Equation (7) contains the assumption that the reactants are sufficiently structurally

similar so that the work terms (and hence K_p) for the homogeneous reactions are essentially constant. Providing that at least one member of a given reaction series (a "reference reaction") occurs via an outer-sphere electrochemical pathway so that k_{et}^{os} can be obtained from Eq. (5), estimates of k_{et}^{os} can be extracted for the remaining reactants by using Eq. (7).

Table V contains estimates of k_{et}^{os} thus obtained for reduction of a number of Co(III) complexes in several reaction environments, all referred to the common potential of 0 mV vs S.C.E. The values labelled $k_{et}^{os,Hg}$ are obtained from the work-corrected rate constants measured in 0.1 M $NaClO_4$ and 0.1 M KPF_6 at mercury electrodes[21,32,35] by using Eq. (5) with $\delta r = 1\text{Å}$, whereas those labelled $k_{et}^{os,Hg}$ were obtained from the values of k_{app} measured at iodide-coated platinum relative to that for $Co(NH_3)_5F^{2+}$ reduction (vide supra). Three entries, labelled $k_{et}^{os,Ru}$, $k_{et}^{os,Cr}$, and $k_{et}^{os,Fe}$ were obtained from the rate constants for homogeneous reduction using $Ru(NH_3)_6^{2+}$, $Cr(bpy)_3^{2+}$ [bpy = 2,2'-bipyridine], and $Fe(CN)_6^{4-}$, respectively, relative to those for $Co(NH_3)_5OH_2^{3+}$ reduction by using Eq. (7), taking k_{et}^{os} for the latter reaction to equal the value obtained at mercury electrodes, 2×10^3 sec^{-1}. (This "reference" reaction was chosen since homogeneous rate data were available with all three reductants. See the footnotes to Table V for the data sources.) Also given for comparison in Table V are the experimental values of k_{et}^{is} for the halide- and pseudohalide-bridged reactions at platinum and gold electrodes, obtained from the data given in Tables I and II.

DISCUSSION

Inspection of the rate parameters in Tables I, II, and V reveals several interesting features. Most prominent is the comparison between the values of k_{et}^{is} for $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5NCS^{2+}$ reduction and the corresponding values of k_{et}^{os} obtained at iodide-coated platinum. For the halide-bridged reactions k_{et}^{is} is markedly (10-100 fold) greater than k_{et}^{os}, whereas for the thiocyanate-bridged

reaction k_{et}^{is} is significantly smaller than k_{et}^{os}. This suggests, not unexpectedly, that the influence of surface attachment upon the electron-transfer energetics is sensitive to the nature of the bridging ligand.

In order to discuss these and other features of the present results it is useful to relate k_{et} to the activation free energy for the elementary step, ΔG^{*}_{et}, by[3a]

$$k_{et} = \kappa_{el}\, \nu_n \exp(-\Delta G^{*}_{et}/RT) \qquad (8)$$

The nuclear frequency factor, ν_n, describes the effective frequency with which the transition state is formed (it is typically close to 1×10^{13} sec^{-1}), whereas electronic transmission coefficient, κ_{el}, describes the fractional probability that electron transfer will occur once the nuclear transition state is formed.

The reorganization barrier ΔG^{*}_{et} can usefully be subdivided as:[2a,3b]

$$\Delta G^{*}_{et} = \Delta G^{*}_{int} + \alpha_{et}[F(E-E^{o}) + RT(\ln K_p - \ln K_s)] \qquad (9)$$

where α_{et} is the transfer coefficient for the electron-transfer step ($\simeq 0.5$), E^{o} is the standard (or formal) potential for the redox couple, K_p and K_s are the equilibrium constants for forming the precursor and successor states from the bulk reactant and product, respectively, and ΔG^{*}_{int} is the so-called intrinsic barrier. This last term is the value of ΔG^{*}_{et} that remains when the free energies of the precursor and successor states are equal; ΔG^{*}_{int} is of particular interest since it is the free-energy barrier usually obtained from contemporary electron-transfer theories. A dependence of k_{et} upon the transition-state geometry or reaction environment for a given electrochemical reaction at a fixed electrode potential may arise either from variations in κ_{el} or from alterations in ΔG^{*}_{et}. The latter may arise from variations in the "surface thermodynamic" term

$RT(\ln K_p - \ln K_s)$ as well as in ΔG^*_{int}.[11a] If the surface binding in the precursor and successor states are similar so that $K_p \simeq K_s$, then the influence of the precursor state stability upon k_{et} will vanish, and will only affect the overall reactivity k_{app} via Eq. (2). These factors are illustrated in Fig. 1 which shows schematic free-energy profiles for a reaction occurring in two different surface environments, yielding the profiles OPASR and OP'A'S'R. A change in ΔG^*_{int} corresponds to a difference in the shapes of the curve PA from P'A', and/or AS from A'S', whereas a change in the "surface thermodynamic" component corresponds simply to a difference in the vertical displacement of P' from P relative to that of S' from S. It is important to note that since k_{et} refer to intramolecular electron transfer within a previously assembled bound state, it will be influenced only by interactions between the redox center and the metal surface, rather than by the nature and strength of the bridging ligand-surface bond. Variations in k_{et} are therefore indicative of alterations in the "degree of communication" between the metal redox center and the electrode surface.

Most likely, then, the greater electron-transfer mediating properties noted above for chloride and bromide bridging ligands, especially relative to thiocyanate, arise either from an ability of the former to enhance electronic coupling between the Co(III) acceptor and metal surface donor orbitals, thereby increasing κ_{el}, or by diminishing ΔG^*_{int} by weakening the cobalt-ligand bonds and/or decreasing the solvent reorganization energy. All these possibilities seem reasonable for halide ligands especially since surface attachment will place the cobalt redox center closer to the metal surface than for both thiocyanate-bridged and for outer-sphere pathways. For the latter the reactant is probably sepa from the electrode by a layer of solvent molecules.[25] The formation of t halide bond could drain electron density from the Co(III)-halide bond, es platinum for which there is evidence that halide-surface bonds are fairly covalent.[36]

By comparison, the influence of the sulfur-surface bond upon the Co(III)-nitrogen bond for bridging thiocyanate should be relatively slight. The significantly smaller values of k_{et}^{is} relative to k_{et}^{os} for thiocyanate-bridged reactions are somewhat puzzling in this regard. It is possible that surface attachment may yield an increase in ligand-field strength at Co(III) caused by π back bonding from the metal surface;[37] this may account for the especially small value of k_{et}^{is} obtained at platinum (Table I). However, a more likely possibility is that the value of δr, 1Å, chosen for the present outer-sphere reactions is an underestimate. This will be the case if the outer-sphere transition state is sufficiently close to the surface so that adiabatic pathways (i.e. $\kappa_{el} \simeq 1$) are achieved not only at the plane of closest approach but also at significantly greater reactant-electrode distances. This point is discussed in detail elsewhere.[38]

Further insight into the structural factors responsible for the observed dependence of k_{et} upon the nature of the bridging ligand as well as the reaction pathway can be obtained by examining the relative values of k_{et}^{os} obtained for the various reaction environments in Table V. A surprising feature is that the estimates of k_{et}^{os} for $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ reduction extracted from the rate of their homogenous reduction by $Ru(NH_3)_6^{2+}$ and $Cr(bpy)_3^{2+}$, $k_{et}^{os,Ru}$ and $k_{et}^{os,Cr}$, are substantially larger than those obtained using either $Fe(CN)_6^{4-}$ or iodide-coated platinum as reaction environments. Indeed, while the values of $k_{et}^{os,PtI}$ and $k_{et}^{os,Fe}$ are fairly insensitive to the nature of the anionic ligand X, the values of $k_{et}^{os,Ru}$ and $k_{et}^{os,Cr}$ display a sensitivity that is comparable or even greater than that found for the corresponding values of k_{et}^{is} at platinum and gold (Table V). The especially facile inner-sphere reduction pathways available to $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ reactants at platinum and gold therefore appear to be matched by those occurring with the outer-sphere reagents $Ru(NH_3)_6^{2+}$ and $Cr(bpy)_3^{2+}$.

This invites speculation that an important factor determining the reactivity of these Co(III) complexes is the orientation of the Co(III)-anion bond with respect to the reducing center. Thus $Fe(CN)_4^{4-}$ and PtI provide negatively charged reduction environments which should tend to orient the coordinated anion away from the reductant, whereas the opposite is expected to be true with the positively charged reductants $Ru(NH_3)_6^{2+}$ and $Cr(bpy)_3^{2+}$ as well as for the inner-sphere electrochemical environments. The interposition of the coordinated anion between the donor and acceptor sites could have a marked influence upon the redox reactivity by altering ΔG^*_{et}, and possibly the transmission coefficient κ_{el}, since the electron is likely to be transferred into a cobalt e_g orbital localized between the redox centers. Therefore a major component of ΔG^*_{et} should be the energy required to stretch the Co(III)-X bond. This energy should be smaller for the weak field ligands Cl^- or Br^- than for the stronger field ligands NCS^- or N_3^-, thus accounting for the larger values of k_{et} with the former ligands (Table V). The much milder ligand effects observed for the outer-sphere reductants $Fe(CN)_6^{4-}$ and PtI are nicely compatible with this notion since the Co(III)-anion bond is less likely to influence the electron mediation when the anion is repelled from the reductant.[39] A markedly greater reactivity of chloride- versus thiocyanate-bridged reactions is also observed for c-$Co(en)_2Cl_2^+$ and c-$Co(NH_3)_4Cl_2^+$ versus c-$Co(en)_2(NCS)_2^+$ electroreductions (Table II), although further interpretation is precluded by the paucity of homogenous reactivity data for these complexes. Therefore the extent of inner-sphere electrocatalysis, as measured by the relative values of k_{et}^{is} and k_{et}^{os} for a given electrode reaction, may be as much influenced by reactant orientation effects as by electronic coupling arising from the formation of the bridging ligand-surface bond.

Although extensive experimental data exist for the homogeneous inner-sphere reduction of Co(III) ammine complexes, quantitative interpreation is hampered by a lack of information on the precursor complex stabilities.[41] Nevertheless, at

least for electron transfer between e_g orbitals, chloride appears to be a more effective bridge than polyatomic ligands such as azide in spite of the relatively low stabilities expected for halide-bridged precursor states.[41]

GENERAL CONCLUSIONS

The reactivity comparisons for corresponding inner- and outer-sphere pathways presented here and in related articles,[2a,3c,11] utilizing unimolecular rate constants k_{et} for the elementary electron-transfer step, represents a promising means for exploring the ways in which attachment of the redox center to the metal surface can influence the kinetics of heterogeneous electron transfer. It is interesting to note that underlying connection between the reaction energetics of inner- and outer-sphere electrode reactions is inherently more direct than that for homogeneous redox reactions since only one redox center is required to be reorganized in the former case. In the latter case, the coordination shell of one reactant must be altered in order to form the binuclear precursor complex, thereby complicating the relationship between k_{et}^{is} and k_{et}^{os}.

The present results illustrate that the effectiveness of the bridging ligand in altering the energetics of the elementary electron-transfer step may be at least as important a factor determining the overall electrocatalysis (i.e. enhancements of k_{app}) as the more commonly considered component due to increases in the cross-sectional reactant concentration of the precursor state (i.e. increases in K_p). The magnitude of the latter factor will generally be limited by the availability of surface coordination sites inasmuch as the values of Γ_p cannot exceed a monolayer, at least for chemisorbed intermediates. It remains to be seen if other polyatomic bridging groups can match the degree of inner-sphere electrocatalyses afforded by chloride and bromide ligands.

ACKNOWLEDGMENTS

We are grateful to Prof. Albert Haim for communicating some unpublished kinetic data for $Fe(CN)_6^{4-}$ reduction. Helpful preliminary experiments were performed by Robert Cave. Frequent discussions with Dr. Kendall Guyer and Joseph Hupp aided the data interpretation. This work is supported by the Air Force Office of Scientific Research and the Office of Naval Research.

REFERENCES AND NOTES

(1) Graduate research assistant, Michigan State University, 1977-81.

(2) (a) Weaver, M. J., Inorg. Chem. 1979, 18, 402; (b) Weaver, M. J., Israel J. Chem. 1979, 18, 35; (c) Guyer, K. L.; Barr, S. W.; Cave, R. J.; Weaver, M. J., in "Proc. 3rd Symp. on Electrode Processes," B. Bruckenstein, J. D. E. McIntyre, B. Miller, E. Yeager (eds.), Electrochemical Society, Princeton, N.J., 1980, p. 390.

(3) (a) Hupp, J. T.; Weaver, M. J., J. Electroanal. Chem., 1983, 152, 1.
(b) Weaver, M. J., in "Inorganic Reactions and Methods," J. J. Zuckerman (ed.) Verlag Chemie, in press.

(4) (a) Sutin, N., in "Bioinorganic Chemistry," Vol. 2, G. L. Eickhorn (ed.), Elsevier, N.Y., 1973, Chapter 19; (b) Haim, A., Acc. Chem. Res. 1975, 8, 264; (c) Brown, G. M.; Sutin, N., J. Am. Chem. Soc. 1979, 101, 883;
(d) Sutin, N.; Brunschwig, B. S., ACS Symp. Ser. 1982, 198, 105.

(5) Weaver, M. J.; Anson, F. C., J. Electroanal. Chem. 1975, 58, 95.

(6) Guyer, K. L.; Barr, S. W.; Weaver, M. J., in "Proc. Symp. on Electrocatalysis," W. E. O'Grady, P. N. Ross, Jr.; F. G. Will (eds.), Electrochemical Society, Pennington, N.J., 1982, p. 377.

(7) For reviews, see (a) Taube, H., Adv. Chem. Ser. 1977, 162, 127; (b) Taube, H., in "Tunneling in Biological Systems," Chance, B.; DeVault, D. C.; Frauenfelder, H.; Marcus, R. A.; Schieffer, J. R.; Sutin, N., Academic Press, N.Y., 1979, p. 173; (c) Haim, A., Prog. Inorg. Chem. 1983, 30, 273.

(8) For example: Zawacky, S. K. S.; Taube, H., J. Am. Chem. Soc. 1981, 103, 3379; Szecsy, A. P.; Haim, A., J. Am. Chem. Soc. 1981, 103, 1679.

(9) (a) Lane, R. F.; Hubbard, A. T.; J. Phys. Chem. 1973, 77, 1401, 1411;
(b) Sharp, M.; Peterson, M.; Edstrom, K., J. Electroanal. Chem. 1979, 95, 123; 1980, 109, 271.

(10) Taube, H., "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, N.Y., 1970.

(11) (a) Weaver, M. J.; Guyer, K. L., submitted (Part II); Li, T.-T.; Liu, H. Y.; Weaver, M. J., submitted (Part III).

(12) Barr, S. W.; Guyer, K. L.; Li, T. T.-T.; Liu, H. Y.; Weaver, M. J., in "Proc. Symp. on the Chemistry and Physics of Electrocatalysis" J.D.E. McIntyre, M. J. Weaver, E. Yeager, eds. Electrochemical Society, in press.

(13) Brauer, G. (ed) "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd Edition, Academic Press, N.Y., 1965, p. 1531.

(14) Basolo, F.; Newmann, R. A., Inorg. Synth. 1946, 4, 171.

(15) Diehl, H.; Clark, H.; Willards, H. H., Inorg. Synth. 1939, 1, 186.

(16) Carlin, R. L.; Edwards, J. O., J. Inorg. Nucl. Chem. 1958, 6, 217.

(17) Hynes, W. A.; Yanowski, L. K.; Shuller, M., J. Am. Chem. Soc., 1938, 60, 3053.

(18) Weaver, A.; Braunlich, F., Z. Anorg. Chem. 1900, 22, 95.

(19) Weaver, A.; Braunlich, F., Z. Anorg. Chem. 1900, 22, 125.

(20) Ref. 13, p. 1536.

(21) Satterberg, T. L.; Weaver, M. J., J. Phys. Chem. 1978, 82, 1784.

(22) Barr, S. W.; Guyer, K. L.; Weaver, M. J., J. Electroanal. Chem. 1980, 111, 41.

(23) Galus, Z., "Fundamentals of Electrochemical Analysis," Ellis Horwood, 1976, p. 236.

(24) Barr, S. W.; Ph.D. Thesis, Michigan State University, 1981.

(25) Weaver, M. J.; Satterberg, T. L., J. Phys. Chem. 1977, 81, 1772.

(26) Lane, R. F.; Hubbard, A. T., J. Phys. Chem. 1975, 79, 808; Clavilier, J.; Huong, N. V., J. Electroanal. Chem. 1973, 41, 193; Hamelin, A.; Dechy, P., Compt. Rend. 1973, C276, 33; Takamura, T.; Takamura, K.; Yeager, E., J. Electroanal. Chem. 1971, 29, 279.

(27) Gilman, S., in "Electroanalytical Chemistry," A. J. Bard, ed., M. Dekker, New York, N.Y., Vol. 2, 1967, p. 113.

(28) This may well be due to distortions of the cathodic voltammograms arising from nonfaradaic currents caused by adsorption of the free anions released upon reduction of the Co(III) adsorbates.[24]

(29) Extensive adsorption of these cationic complexes is also indicated by the rate decreases that addition of their Cr(III) analogs induces upon "outer-sphere probe" reactions, such as $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5F^{2+}$ reduction, at platinum and gold.[24]

(30) The "bulk" reactant concentrations C_r are those just beyond the double layer, i.e. those corrected for diffusion polarization.

(31) Marcus, R. A., J. Chem. Phys. 1965, 43, 679; J. Phys. Chem. 1963, 67, 853.

(32) Weaver, M. J., J. Electroanal. Chem. 1978, 93, 231.

(33) The values of k_{app} for $Co(NH_3)_5F^{2+}$ reduction at iodide-coated platinum in the vicinity of 0 mV vs S.C.E. were typically ca. 30-fold larger than the double-layer corrected values obtained at mercury.[22,32] This rate difference is consistent with diffuse-layer potentials ϕ_d of about -70 mV at the former surface. Similar values of ϕ_d were also obtained using $Co(NH_3)_6^{3+}$ reduction as a kinetic probe.[24] Such negative values are consistent with the presence of a partial negative charge on the adsorbed iodide.

(34) Marcus, R. A., J. Chem. Phys. 1965, 43, 679.

(35) Weaver, M. J., unpublished data.

(36) Frumkin, A. N.; Petry, O. A., Electrochim. Acta 1970, 15, 391.

(37) (a) Frank, S. N.; Anson, F. C., J. Electroanal. Chem. 1974, 54, 55; (b) Barclay, D. J.; Passeron, E.; Anson, F. C., Inorg. Chem., 1970, 9, 1024.

(38) Hupp, J. T.; Weaver, M. J., submitted for publication.

(39) It should be borne in mind that the expected sensitivity of k_{et} to the nature of the ligand environment will be determined in part by their influence upon E^{o} of the redox couple [Eqs. (8), (9)]. Unfortunately, values of E^{o} are unknown for the present Co(III)/(II) reactions on account of the substitution lability and instability of the Co(II) products. Nevertheless, rough estimates of the ligand dependence of k_{et} for $Co^{III}(NH_3)_5X$ reductions from stability constant data indicate that up to 20-fold larger k_{et} values for $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ reduction might be expected relative to $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5NCS^{2+}$ reduction on this basis.[12]

(40) Guyer, K. L., Ph.D. Thesis, Michigan State University, 1981.

(41) Linck, R. G., in "MTP International Review of Science," Inorg. Chem. Series I, Vol. 9, Butterworths, London, 1972, p. 303.

(42) Gaswick, D.; Haim, A., J. Am. Chem. Soc. 1971, 93, 7347.

TABLE I -- Comparisons of Rate Parameters for Inner- and Outer-Sphere Pathways for the Reduction of Some Pentaamminecobalt (III) Complexes at Platinum, Gold, Silver, and Mercury Electrodes in 0.1 M $NaClO_4$ + 5 mM $HClO_4$ at 24°C.

Reactant	Surface[a]	E mV vs. s.c.e.	Mechanism[b]	C_r[c] mM	Γ_p[d] 10^{11} mole cm^{-2}	k_{app}[e] cm sec^{-1}	α_{app}[f]	K_p^0[g] cm	k_{et}^{is}[h] sec^{-1}	k_{et}^{os}[i] sec^{-1}
$Co(NH_3)_5Cl^{2+}$	Pt	300	i.s.	0.50	~40	7×10^{-3}	0.60	8×10^{-4}	9	
	Pt	"	i.s.		10-30				*33*	
	Au	"	i.s.	~ 0.05	~ 30	~ 0.1	0.60	6×10^{-3}	~ 15	
	Ptl	"	o.s.	1.0		1.5×10^{-7}	0.66			~ 0.4
	Aul	"	o.s.	1.0		~ 1×10^{-7}	0.63			
$Co(NH_3)_5Br^{2+}$	Pt	300	i.s.	0.15	40	2×10^{-2}	0.62	3×10^{-3}	5	
	Au	"	i.s.	~ 0.04	~ 30	~ 0.15	0.7	~ 8×10^{-3}	~ 20	
	Ptl	"	o.s.	1.0		~ 4×10^{-8}	0.68			~ 0.2
	Aul	"	o.s.	1.0		~ 1×10^{-7}	0.66			
$Co(NH_3)_5NCS^{2+}$	Pt	0	i.s.	0.9	25	4×10^{-4}	0.36	3×10^{-4}	1.5	
	Au	"	i.s.	0.1	25	5×10^{-2}	0.58	2.5×10^{-3}	20	
	Au	"	i.s.		10-20				*35*	
	Ag	"	i.s.	0.2	25 [k]	2×10^{-2} [k]	~ 0.7	1×10^{-3}	20	
	Hg	"	i.s.	0.5	~ 2 [j]	~ 1×10^{-3} [j]	0.7	~ 4×10^{-5}	~ 25	
	Ptf	"	o.s.	*1.0*		2×10^{-4}	0.4			~ 100
	Auf	"	?	0.2		2.5×10^{-2}	0.55			

[a] Ptl and Aul refer to platinum and gold surfaces in contact with 0.1 M $NaClO_4$ + 5 mM $HClO_4$ containing 5 mM NaF.

[b] i.s. = inner-sphere mechanism; o.s. = outer-sphere mechanism.

[c] Reactant concentration in vicinity of electrode to which quoted value of k_{app} refers, i.e. bulk concentration corrected for concentration polarization (see text).

[d] Surface reactant concentration for ligand-bridged intermediate corresponding to quoted electrode potential and C_r, estimated using rapid linear sweep voltammetry (see text), except where noted.

[e] Apparent rate constant, determined from $k_{app} = i_c/FC_r$, where i_c is the cathodic current density.

[f] Apparent transfer coefficient, determined from $\alpha_{app} = (-RT/F)(\partial \ln k_{app}/\partial E)$.

[g] Formal equilibrium constant for formation of adsorbed (precursor) intermediate under stated conditions. Determined from $K_p = \Gamma_p/C_r$.

[h] Unimolecular surface rate constant for inner-sphere reactions, determined from k_{app} using $k_{et}^{is} = k_{app}/K_p$ [Eqn. (2)], except those in italics which were determined directly using rapid linear sweep voltammetry (see text and ref. 11a).

[i] Unimolecular surface rate constant for outer-sphere pathway, corrected for electrostatic double-layer effects, obtained from k_{app} using Eqns. (5) and (6) assuming that $\delta r = 1\text{Å}$ (see text).

[j] Data taken from ref. 2a.

[k] Data taken from ref 40.

TABLE II -- Rate Parameters for the Electrochemical Reduction of Some Co(III) Complexes Expected to Follow Dibridged Inner-Sphere Pathways.

Reactant	Surface[a]	E mV vs. s.c.e.	C_T[c] mM	Γ_p[d] 10^{11} mole cm^{-2}	k_{app}[e] cm sec^{-1}	α_{app}[f]	K_p[g] cm	k^{1s}_{et}[h] sec^{-1}
o-$Co(NH_3)_4Cl_2^+$	Pt	300	0.15	~ 30	2.5×10^{-2}	0.48	2×10^{-3}	12.5
	Au	"	0.6	~ 30	4×10^{-3}	0.62	5×10^{-4}	8
	Pt(I)	"	1.0		1×10^{-5}	0.58		
	Au(I)	"	1.0		1×10^{-5}	0.58		
o-$Co(en)_2Cl_2^+$	Pt	300	1.0	~ 30	3×10^{-4}	0.58	3×10^{-4}	1.0
	Au	"	0.6	~ 30	5×10^{-3}	0.59	5×10^{-4}	10
	Pt(I)	"	1.0		4×10^{-6}	0.40		
	Au(I)	"	1.0		7×10^{-6}	0.57		
o-$Co(en)_2NCS)_2^+$	Pt	0	1.0	25	1×10^{-4}	0.58	3×10^{-4}	0.3
	Au	"	1.0	25	6.5×10^{-4}	0.64	3×10^{-4}	2
	Au	"		10-25				6
	Ag	"	1.0	~ 25	1×10^{-3}[i]	~ 0.6[i]	3×10^{-4}	3
	Ag	"		~ 10				6[i]
	Hg	"		5-15		0.6		0.02
	Pt(I)	"	1.0		1.5×10^{-4}	0.58		
	Au(I)	"	1.0		1×10^{-4}	0.5		

For footnotes, see Table I.

TABLE III -- Reaction Orders for the Reduction of Selected Co(III) Ammine and Ethylenediamine Complexes

Reactant	← Reaction Order → Pt[b]	PtI[c]	Au[b]	AuI[c]
$Co(NH_3)_5Cl^{2+}$	0.15[d]	1.0[e]	0.10[d]	1.05[e]
$Co(NH_3)_5Br^{2+}$	0.4[d]	0.85[e]	0.4[d]	1.0[e]
$Co(NH_3)_5NCS^{2+}$	0.4[f]	0.9[f]	0.35[f]	0.85[f]
c-$Co(en)_2(NCS)_2^+$	0.5[f]		0.25[f]	
$Co(NH_3)_5OH_2^{3+}$	1.05[f]	0.9[f]	0.9[f]	0.95[f]

[a] Determined using rotating disk voltammetry for reactant concentrations in the range ca 0.1 - 1 mM (see text).

[b] Determined in 0.1 M $NaClO_4$ + 5 mM $HClO_4$.

[c] Determined in 0.1 M $NaClO_4$ + 5 mM $HClO_4$ + 5 mM NaI.

[d] At 400 mV.

[e] At 250 mV.

[f] At 0 mV.

TABLE IV -- Specific Adsorption of Some Co(III) Reactants at Platinum and Gold Electrodes as Determined by Rapid Linear Sweep Voltammetry.

Complex	Surface[a]	C_r[b] mM	E_i[c] mV vs. s.c.e.	ν[d] V sec^{-1}	$\Gamma_p \times 10^{11}$[e] mole cm^{-2}	E_p[f] mV vs. s.c.e.
$Co(NH_3)_5Cl^{2+}$	Pt	0.02	500-700	10	38	120
		0.08	"	10	40	145
$Co(NH_3)_5NCS^{2+}$	Au	0.03	200-400	10	19	-145
		0.05	"	10	20	-145
c-$Co(en)_2(NCS)_2^+$	Au	0.01	200-400	10	19	-300
		0.01	"	20	20	-300
		0.05	"	20	24	-300
		0.10	"	20	26	-300

[a] Electrolyte was 0.1 M $NaClO_4$ + 5 mM $HClO_4$ in each case.

[b] Bulk reactant concentration

[c] Initial (equilibrium) potential preceding potential sweep.

[d] Cathodic sweep rate.

[e] Surface reactant concentration at E_i, determined from charge under voltammetric peak (see refs. 6, 11a, and 40 for details).

[f] Electrode potential corresponding to voltammetric peak.

TABLE V — Unimolecuar Rate Constants (sec^{-1}) for Reduction of $Co^{III}(NH_3)_5X$ Complexes Containing Inorganic Bridging Ligands X at 0 mV vs. s.c.e.

	← Electrochemical →				← Homogenous →		
Reactant	$k_{et}^{os,Hg}$ [a]	$k_{et}^{os,PtI}$ [b]	$k_{et}^{is,Pt}$ [c]	$k_{et}^{is,Au}$ [d]	$k_{et}^{os,Ru}$ [e]	$k_{et}^{os,Cr}$ [e]	$k_{et}^{os,Fe}$ [e]
$Co(NH_3)_5OH_2^{3+}$	2×10^3				$[2 \times 10^3]$	$[2 \times 10^3]$	$[2 \times 10^3]$
$Co(NH_3)_6^{3+}$	10	~ 10			6		
$Co(NH_3)_5F^{2+}$	1×10^2	$[1 \times 10^2]$			2×10^2		
$Co(NH_3)_5Cl^{2+}$		2×10^2	3×10^3	6×10^3	2×10^5	3×10^4	3×10^2
$Co(NH_3)_5Br^{2+}$		2×10^2	1.5×10^3	8×10^3	1×10^6	2×10^5	
$Co(NH_3)_5NCS^{2+}$		1×10^2	1.5	30	5×10^2	4×10^2	50
$Co(NH_3)_5N_3^{2+}$						1.5×10^3	25

[a] Unimolecular rate constants for outer-sphere pathways at mercury electrodes, obtained from values of k_{app} in 0.1 M $NaClO_4$ and/or 0.1 M KPF_6 [21,32,35] by applying work term corrections as in ref. 32 and using Eq (5) with $\delta r = 1$Å.

[b] Outer-sphere unimolecular rate constants at iodide-coated platinum surface. Obtained from $k_{et}^{os,PtI} = (k_{app,X}^{PtI}/k_{app,F}^{PtI})\, k_{et,F}^{os,Hg}$, where subscripts X and F refer to rate constants obtained for reduction of the given $Co^{III}(NH_3)_5X$ complex and for $Co(NH_3)_5F^{2+}$, respectively.

[c] Inner-sphere unimolecular rate constants at platinum electrodes, taken from Table I; values for $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ reduction extrapolated from 300 to 0 mV assuming that $\alpha_{et} = 0.5$.

[d] As for footnote c, but at gold electrodes.

[e] Outer-sphere unimolecular rate constants estimated from rate data for homogenous reduction by $Ru(NH_3)_6^{2+}$ using Eq. (7), with $Co(NH_3)_5OH_2^{3+}$ reduction as the "reference reaction," with $k_{et,2}^{os}$ taken as the value, 2×10^3 sec^{-1}, obtained at mercury (see Table V).

[f] As for footnote e, but for $Cr(bpy)_3^{2+}$ reduction.

[continued on next page]

[g] As for footnote f, but for $Fe(CN)_6^{4-}$ reduction. [Note that very similar values of $k_{et}^{os,Fe}$ were obtained using the unimolecular rate constants for $Fe(CN)_6^{4-}$ reduction[42] as with the conventional bimolecular rate data.]

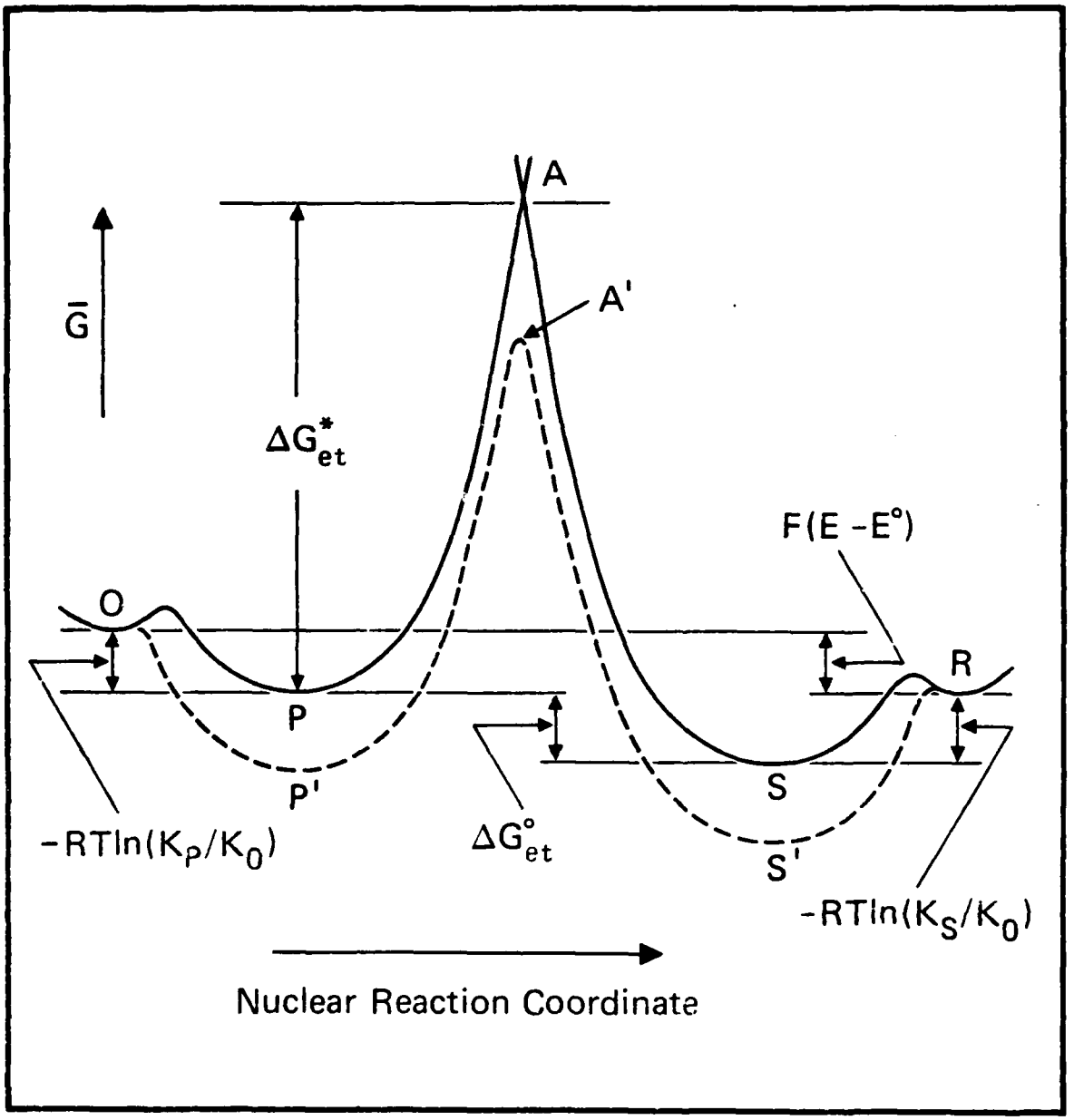
Literature sources of homogenous rate data used to obtain $k_{et}^{os,Ru}$, $k_{et}^{os,Cr}$, and $k_{et}^{os,Fe}$ as follows.

$Ru(NH_3)_6^{2+}$ reductions: X = OH_2, NH_3, Cl^-, Br^-, Endicott, J. F.; Taube, H., J. Am. Chem. Soc. 1964, 86, 1686; X = F^-, Patel, R. C.; Endicott, J. F., J. Am. Chem. Soc. 1968, 90, 6364; X = NCS^-, N_3^-, Adegite, A.; Dosumu, M.; Ojo, J. F., J. Chem. Soc. Dalton, 1977, 630.

$Cr(bpy)_3^{2+}$ reductions: Candlin, J. P.; Halpern, J.; Trimm, D. L., J. Am. Chem. Soc. 1964, 86, 1019.

$Fe(CN)_6^{4-}$: X = OH_2, ref. 42; X = Cl^-, NCS^-, N_3^-, Mirralles, A.; Ph.D. Thesis, State University of New York at Stoneybrook, 1974; Haim, A.; personal communication.

Figure 1.


A
A'
$\bar{G}$
ΔG^*_{et}
F(E -E°)
O
R
P
P'
S
S'
$-RT\ln(K_P/K_0)$
ΔG°_{et}
$-RT\ln(K_S/K_0)$
Nuclear Reaction Coordinate

Caption to Figure 1

Schematic free energy-reaction coordinate profile for a one-electron electroreduction occurring via two different reaction pathways (or surface environments) at a given electrode potential E. Key: O, bulk reactant state; P,P', precursor states; A,A', activated states; S,S', successor states; R, bulk product state. See text for further labelling details.